CLAIMS

1. A process for producing a (poly)ol block copolymer comprising the reaction of a DMC catalyst with a polycarbonate or polyester (poly)ol (co)polymer and ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

2. A process for producing a (poly)ol block copolymer comprising a first reaction in a first reactor and a second reaction in a second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol copolymer of the first reaction, ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer, wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

3. A process according to claim 1 or 2, wherein the polycarbonate or polyester (poly)ol (co)polymer is added to pre-activated DMC catalyst.

4. A process according to any of claims 1 to 3, wherein the polycarbonate or polyester (poly)ol (co)polymer is added to the DMC, ethylene oxide and optionally other alkylene oxides reaction mixture.

5. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer is added to the DMC catalyst continuously or semi-continuously, preferably the polycarbonate or polyester (poly)ol (co)polymer is added continuously.

6. A process according to any preceding claim, wherein at least a separate portion of the polycarbonate or polyester (poly)ol (co)polymer is added after the start of the reaction.

7. A process according to any preceding claim, wherein the DMC catalyst is pre-activated with a starter compound, or the polycarbonate or polyester (poly)ol (co)polymer, or with the (poly)ol block copolymer product.

8. A process according to any preceding claim, wherein > 75%, more preferably, >80% of the (poly)ol block copolymer chain ends are terminated by primary hydroxyl groups.

9. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer is fed into the reaction with the DMC catalyst continuously or semi-continuously, as a crude reaction mixture, wherein said reaction contains a pre-activated DMC catalyst.

10. A process according to claim 9, wherein the crude reaction mixture fed into the reaction with the DMC catalyst includes an amount of unreacted ethylene oxide and/or other alkylene oxide and/or starter.

11. A process according to any preceding claim, wherein the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, $C_{11}H_{22}O$), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides, preferably propylene oxide.

12. A process according to any preceding claim, wherein when one or more other alkylene oxides are added to the reaction with the DMC catalyst in addition to ethylene oxide, the ethylene oxide addition is increased mol/mol relative to the other alkylene oxide(s) at the end part of the reaction.

13. A process according to any preceding claim, wherein the reaction with the DMC catalyst is carried out substantially in the absence of CO_2.

14. A process according to any preceding claim, wherein ethylene oxide forms 5-100% mol/mol of the alkylene oxides added to the reaction with the DMC catalyst, more typically, 10-100%, most typically 10-50% mol/mol of the alkylene oxides added, and/or, at least 5%, 10%, 15%, 20%, 25% or 30% mol/mol of the alkylene oxides added.

15. A process according to any preceding claim, wherein the alkylene oxide residues in the polycarbonate or polyester (poly)ol are ethylene oxide and/or propylene oxide residues and optionally, in addition, other alkylene oxide residues.

16. A process according to any preceding claim, wherein at least 50% of the alkylene oxide residues of the polycarbonate or polyester (poly)ol are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels.

17. A process according to claim 15, wherein the other alkylene oxide residues are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, C10H16O or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, C11H22O), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

18. A process according to any preceding claim, wherein the ethylene oxide and/or optionally alkylene oxide and/or DMC is added continuously or semi-continuously to the reaction with the DMC catalyst.

19. A process according to any preceding claim, wherein the reaction temperature of the reaction with the DMC catalyst is in the range from 50 to 160°C, preferably in the range from 70 to 140°C, more preferably from 80 to 130°C.

20. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer further comprises ether linkages.

21. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer has less than 24% ether linkages, more typically, less than 20% ether linkages, most typically, less than 15% ether linkages.

22. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer has at least 1% ether linkages, more typically, at least 3% ether linkages, most typically, at least 5% ether linkages.

23. A process according to any preceding claim, wherein the polycarbonate or polyester (poly)ol (co)polymer has between 1% and 25% ether linkages, typically between 5% and 20% ether linkages, more typically, between 10% and 15% ether linkages.

24. A process according to any preceding claim, wherein the DMC catalyst is pre-activated, in the reactor or separately, optionally wherein the DMC is pre-activated with a starter compound or with the polycarbonate (poly)ol (co)polymer or the (poly)ol block copolymer product.

25. A process according to any preceding claim, wherein the DMC catalyst, in addition to at least two metal centres and cyanide ligands, also comprises at least one of: one or more

complexing agents, water, a metal salt and/or an acid, optionally in non-stoichiometric amounts.

26. A process according to any preceding claim, wherein the DMC catalyst is prepared by treating a solution of a metal salt with a solution of a metal cyanide salt in the presence of at least one of: complexing agent, water, and/or an acid, optionally wherein the metal salt is of the formula M'(X')p, wherein M' is selected from Zn(II), Ru(II), Ru(III), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(VI), Sr(II), W(IV), W(VI), Cu(II), and Cr(III),

X' is an anion selected from halide, oxide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate,

p is an integer of 1 or more, and the charge on the anion multiplied by p satisfies the valency of M'; the metal cyanide salt is of the formula $(Y)_qM''(CN)_b(A)_c$, wherein M'' is selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), and V(V),

Y is a proton or an alkali metal ion or an alkaline earth metal ion (such as K+),

A is an anion selected from halide, oxide, hydroxide, sulphate, cyanide oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate;

q and b are integers of 1 or more;

c may be 0 or an integer of 1 or more;

the sum of the charges on the anions Y, CN and A multiplied by q, b and c respectively (e.g. Y x q + CN x b + A x c) satisfies the valency of M'';

the at least one complexing agent is selected from a (poly)ether, a polyether carbonate, a polycarbonate, a poly(tetramethylene ether diol), a ketone, an ester, an amide, an alcohol, a urea or a combination thereof,

optionally wherein the at least one complexing agent is selected from propylene glycol, polypropylene glycol, (m)ethoxy ethylene glycol, dimethoxyethane, tert-butyl alcohol, ethylene glycol monomethyl ether, diglyme, triglyme, methanol, ethanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol and sec-butyl alcohol, 3-buten-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, 3-methyl-1-pentyn-3-ol, or a combination thereof; and

wherein the acid, if present, has the formula H_rX''', where X''' is an anion selected from halide, sulfate, phosphate, borate, chlorate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate, and r is an integer corresponding to the charge on the counterion X'''.

27. A process according to any preceding claim, wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g$$

wherein M' and M'' are as defined in claim 24, and d, e, f and g are integers, and are chosen such that the DMC catalyst has electroneutrality,

optionally, d is 3, e is 1, f is 6 and g is 2.

28. A process according to any preceding claim, wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g \cdot hM'''X''_i \cdot jR^c \cdot kH_2O \cdot lH_rX'''$$

wherein M', M'', d, e, f and g are as defined in claim 24, M''' is M' and/or M'', X'' is an anion selected from halide, oxide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate, i is an integer of 1 or more, and the charge on the anion X'' multiplied by i satisfies the valency of M''', h, j, k and l are each independently zero or a positive number, r is an integer that corresponds to the charge on the counterion X''', and R^c is a complexing agent or a combination of one or more complexing agents.

29. A process according to any preceding claim, wherein the DMC catalyst is based upon $Zn_3[Co(CN)_6]_2$ (zinc hexacyanocobaltate).

30. A process according to any preceding claim, wherein the DMC catalyst is zinc hexacyanocobaltate and the one or more ligands are selected from alcohols and polyols.

31. A process according to claim 26, wherein the one or more complexing agents are selected from dimethoxyethane, tert-butyl alcohol, polyethylene glycol, polypropylene glycol, polyethercarbonate, poly(tetramethylene glycol), polycarbonate.

32. A process according to any preceding claim, wherein the polycarbonate (poly)ol copolymer is a low molecular weight polycarbonate (poly)ol product having a molecular weight (Mn) in the range 200 to 4000 Daltons as measured by Gel Permeation Chromatography (GPC).

33. A process according to any preceding claim, wherein the polycarbonate (poly)ol copolymer is a generally alternating polycarbonate (poly)ol.

34. A process for producing a (poly)ol block copolymer according to claims 2-33, wherein the starter compound has the formula (III):

$$Z\text{-}(R^Z)_a \qquad \text{(III)}$$

wherein Z can be any group which can have 1 or more, typically, 2 or more $–R^Z$ groups attached to it and may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, hererocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or Z may be a combination of any of these groups, for example Z may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group;

a is an integer which is at least 1, typically, at .least 2,optionally a is in the range of between 1 or 2 and 8, optionally a is in the range of between 2 and 6;

wherein each R^Z may be –OH, -NHR', –SH, -C(O)OH, -P(O)(OR')(OH), $–PR'(O)(OH)_2$ or –PR'(O)OH, optionally R^Z is selected from –OH, -NHR' or -C(O)OH, optionally each R^z is –OH, -C(O)OH or a combination thereof (e.g. each R^z is –OH);

wherein R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, optionally R' is H or optionally substituted alkyl; and

wherein Z' corresponds to R^z, except that a bond replaces the labile hydrogen atom.

35. A process for producing a (poly)ol block copolymer according to claim 34, wherein the starter compound is selected from monofunctional starter substances such as alcohols, phenols, amines, thiols and carboxylic acid, for example, alcohols such as methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, linear or branched C_3-C_{20}-monoalcohol such as tert-butanol, 3-buten-1-ol, 3-butyn-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, propargyl alcohol, 2-methyl-2-propanol, 1-tert-butoxy-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, 1-heptanol, 2-heptanol, 3-heptanol, 1-octanol, 2-octanol, 3-octanol, 4-octanol, 1-decanol, 1-dodecanol, phenol, 2-hydroxybiphenyl, 3-hydroxybiphenyl, 4-hydroxybiphenyl, 2-hydroxypyridine, 3-hydroxypyridine, and 4-hydroxypyridine, mono-ethers or esters of ethylene, propylene, polyethylene, polypropylene glycols such as ethylene glycol mono-methyl ether and propylene glycol mono-methyl ether, phenols such as linear or branched C_3-C_{20} alkyl substituted phenols, for example nonyl-phenols or octyl phenols, monofunctional carboxylic acids such as formic acid, acetic acid, propionic acid and butyric acid, fatty acids, such as stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, benzoic acid and acrylic acid, and monofunctional thiols such as ethanethiol, propane-1-thiol, propane-2-thiol, butane-1-thiol, 3-methylbutane-1-thiol, 2-butene-1-thiol, and thiophenol, or amines such as butylamine, tert-butylamine, pentylamine, hexylamine, aniline, aziridine, pyrrolidine, piperidine, and morpholine; and/or selected from diols such as 1,2-ethanediol (ethylene glycol), 1-3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol,

cyclohexenediol, 1,4-cyclohexanedimethanol, dipropylene glycol, diethylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, polypropylene glycols (PPGs) or polyethylene glycols (PEGs) having an Mn of up to about 1500g/mol, such as PPG 425, PPG 725, PPG 1000 and the like, triols such as glycerol, benzenetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, trimethylol propane, polyethylene oxide triols, polypropylene oxide triols and polyester triols, tetraols such as calix[4]arene, 2,2-bis(methylalcohol)-1,3-propanediol, erythritol, pentaerythritol or polyalkylene glycols (PEGs or PPGs) having 4–OH groups, polyols, such as sorbitol or polyalkylene glycols (PEGs or PPGs) having 5 or more –OH groups, or compounds having mixed functional groups including ethanolamine, diethanolamine, methyldiethanolamine, and phenyldiethanolamine.

36. A process according to any of claims 2-34, wherein the alkylene oxide is asymmetric and wherein the first reaction produces a polycarbonate having between 40-100% head to tail linkages, preferably more than 70%, more than 80% or more than 90% head to tail linkages.

37. A process according to any of claims 2-36, wherein the first reaction is carried out under CO_2 pressure of less than 20 bar, more preferably, less than 10 bar, most preferably, less than 8 bar.

38. A process according to any of claims 2-37, wherein the CO_2 is added continuously in the first reaction.

39. A process according to any of claims 2-38, wherein the first reaction is a batch, semi-batch, or continuous process.

40. A process according to any of claims 2-39, wherein the reactors are located in series.

41. A process according to any of claims 2-39, wherein the reactors are nested.

42. A process according to any of claims 2-41, wherein the first and second reactors are effective to provide different reaction conditions, such as temperature and/or pressure, to each other simultaneously.

43. A process according to any of claims 2-42, wherein the process employs a total amount of alkylene oxide, and wherein 1 to 100% of the total amount of alkylene oxide is mixed in the first reaction, with any remainder added in the second reaction; optionally with 5 to 90% being mixed in the first reaction, optionally with 10 to 90%, optionally with 20 to 90%, optionally with 40 to 90%, optionally with 40 to 80%, optionally with 5 to 50%.

44. A process according to any of claims 4-43, wherein the carbonate catalyst is present in the crude reaction mixture.

45. A process according to any of claims 4-43, wherein the carbonate catalyst has been removed from the crude reaction mixture prior to the addition to the reactor or second reactor.

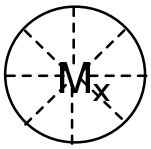
46. A process according to any of claims 2-45, wherein the temperature of reaction in the first reactor is in the range 0°C to 250 °C, preferably from 40 °C to 160 °C, more preferably from 50 °C to 120 °C.

47. A process according to any of claims 2-46 wherein the carbonate catalyst is a catalyst capable of producing polycarbonate chains with greater than 76% carbonate linkages.

48. A process according to any of claims 2-47, wherein the carbonate catalyst is a metal catalyst comprising phenol or phenolate ligands.

49. A process according to any of claims 2-48, wherein the carbonate catalyst is a bimetallic complex comprising phenol or phenolate ligands.

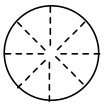
50. A process according to any of claims 2-49 wherein the carbonate catalyst is a catalyst of Formula (IV):



(IV)

Wherein M is a metal cation represented by M-(L)v;

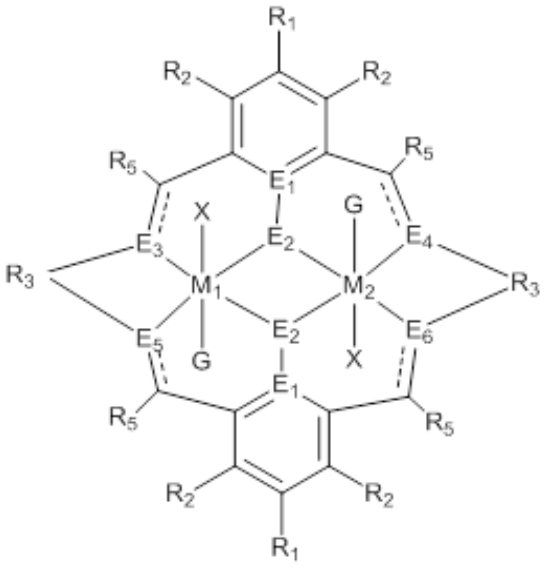
x is an integer from 1 to 4,

 is a multidentate ligand or plurality of multidentate ligands;

L is a coordinating ligand;

v is an integer that satisfies the valency of M, and/or the preferred coordination geometry of M or is such that the complex represented by formula (IV) above has an overall neutral charge.

51. A process according to any of claims 2-50, wherein the carbonate catalyst has the following structure:



(V)

wherein M1 and M2 are independently selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Mg(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Ni(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-(X)2 or Ti(IV)-$(X)_2$;

R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_5 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

E_3, E_4, E_5 and E_6 are selected from N, NR4, O and S, wherein when E_3, E_4, E_5 or E_6 are N, ------ is ═══ , and wherein when E_3, E_4, E_5 or E_6 are NR_4, O or S, ------ is ——— ;

R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR19 or -alkylC≡N or alkylaryl;

X is independently selected from $OC(O)R_x$, OSO_2R_x, $OSOR_x$, $OSO(R_x)_2$, $S(O)R_x$, OR_x, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, amido or optionally substituted

aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl, wherein each X may be the same or different and wherein X may form a bridge between M1 and M2;

Rx is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl; and

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base.

52. A process according to any of claims 2-51, wherein the carbonate catalyst is selected from catalysts of formula (IV), metal salen catalysts, metal porphyrin catalysts, metal tetraaza annulene catalysts and metal beta-diiminate catalysts as defined herein.

53. A process according to any of claims 2-52, wherein the product of the first reaction is used to pre-activate the DMC catalyst in the second reaction, prior to addition of ethylene oxide and optionally, alkylene oxide.

54. A process according to any of claims 2-53, wherein the same or different alkylene oxides are used in the first or second reactions.

55. A process according to any preceding claim, further comprising a reaction comprising the reaction of the (poly)ol block copolymer with a monomer or further polymer to produce a higher polymer.

56. A process according to claim 55, wherein the monomer or further polymer is a (poly)isocyanate and the product of the reaction is a polyurethane.

57. A (poly)ol block copolymer obtainable by the process according to claims 1-56, comprising a general structure B-A-(B)n wherein block A is a polycarbonate or polyester block, wherein n=t-1 and t = the number of reactive end residues on block A, wherein block B is a polyether block and wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

58. A (poly)ol block copolymer obtained by the process according to claims 1-56, comprising a general structure B-A-(B)n wherein block A is a polycarbonate or polyester block, wherein n=t-1 and t = the number of reactive end residues on block A, wherein block B is a polyether block and wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

59. A (poly)ol block copolymer according to claim 57 or 58, wherein > 75%, more preferably, >80% of the copolymer chain ends are terminated by primary hydroxyl groups.

60. A (poly)ol block copolymer according to any of claims 57-59, wherein the mol/mol ratio of block A to block B is in the range 25:1 to 1:250.

61. A (poly)ol block copolymer according to any of claims 57-60, wherein the carbonates present in block A are derived from CO_2.

62. A (poly)ol block copolymer according to any of claims 57-61, wherein block A is derived from alkylene oxides and CO_2.

63. A (poly)ol block copolymer according to any of claims 57-62, wherein block A is partly derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, $C_{11}H_{22}O$), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

64. A (poly)ol block copolymer according to any of claims 57-63, wherein block A is a polyalkylenecarbonate block, more typically derived from alkylene oxides and CO_2.

65. A (poly)ol block copolymer according to any of claims 61-64, wherein the alkylene oxides and CO_2 provide at least 90% of the residues in the block not including any starter, especially, at least 95% of the residues in the block, more especially, at least 99% of the residues in the block, most especially, about 100% of the residues in the block not including any starter are residues of alkylene oxide and CO_2.

66. A (poly)ol block copolymer according to any of claims 62-65, wherein the block A alkylene oxide residues are ethylene oxide and/or propylene oxide residues and optionally, in addition, other alkylene oxide residues.

67. A (poly)ol block copolymer according to any of claims 62-66, wherein at least 50% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels.

68. A (poly)ol block copolymer according to any of claims 57-67, wherein block B has less than 10% carbonate linkages, typically, less than 5% carbonate linkages, more typically, less than 1% carbonate linkages, most typically, 0 % carbonate linkages.

69. A (poly)ol block copolymer according to any of claims 57-68, wherein block A further comprises ether linkages.

70. A (poly)ol block copolymer according to any of claims 57-69, wherein block A has less than 24% ether linkages, more typically, less than 20% ether linkages, most typically, less than 15% ether linkages.

71. A (poly)ol block copolymer according to any of claims 57-70, wherein block A has at least 1% ether linkages, more typically, at least 3% ether linkages, most typically, at least 5% ether linkages.

72. A (poly)ol block copolymer according to any of claims 57-71, wherein block A has between 1% and 25% ether linkages, typically between 5% and 20% ether linkages, more typically, between 10% and 15% ether linkages.

73. A (poly)ol block copolymer according to any of claims 62-72, wherein the alkylene oxide is asymmetric and the polycarbonate or polyester has between 40-100% head to tail linkages, preferably more than 50% head to tail linkages.

74. A (poly)ol block copolymer according to any of claims 57-73, wherein the A block has a high carbonate content and the B block a low carbonate content, for example, the A block has greater than 70% carbonate linkages and/or, for example, the B block has less than 10% carbonate linkages, typically, less than 5% carbonate linkages, more typically, less than 1% carbonate linkages, most typically, 0 % carbonate linkages.

75. A (poly)ol block copolymer according to any of claims 57-74, wherein block B is at least 90% derived, typically, at least 95% derived, more typically, at least 99%, most typically, 100% derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, $C_{11}H_{22}O$), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

76. A (poly)ol block copolymer according to claim 75, wherein ethylene oxide residues form 5-100% of the alkylene oxide residues in block B, more typically, 10-100%, most typically

10-50% of the alkylene oxide residues in block B, and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in block B are ethylene oxide residues.

77. A (poly)ol block copolymer according to claim 75 or 76, wherein at least 5% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, more typically, at least 10% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, most typically, at least 20% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, optionally, at least 50% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, most especially, at least 70 or 90% of the alkylene oxide residues of block B are ethylene or propylene oxide residues.

78. A (poly)ol block copolymer according to any of claims 57-77, wherein at least 70% of the terminal alkylene oxide residues are ethylene oxide residues, more typically, at least 75%, most typically, at least 80% of the terminal alkylene oxide residues are ethylene oxide residues.

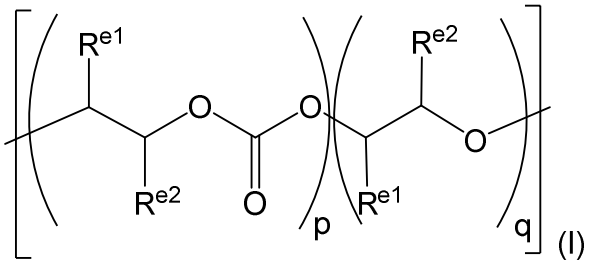
79. A (poly)ol block copolymer according to any of claims 57-78, wherein ethylene oxide residues form 0-100% of the alkylene oxide residues in the (poly)ol block copolymer, typically 5-70%, more typically, 10-60% of the alkylene oxide residues in the (poly)ol block copolymer, most typically, 10-40% of the alkylene oxide residues in the (poly)ol block copolymer, and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in the (poly)ol block copolymer are ethylene oxide residues.

80. A (poly)ol block copolymer according to any of claims 57-79, wherein the (poly)block structure of the copolymer is defined as:

$$B\text{-}A'\text{-}Z'\text{-}Z\text{-}(Z'\text{-}A'\text{-}B)_n$$

wherein n= t-1 and wherein t= the number of terminal OH group residues on the block A; and wherein each A' is independently a polycarbonate chain having at least 70% carbonate linkages, and wherein each B is independently a polyether chain; and wherein Z'-Z-(Z')n is a starter residue.

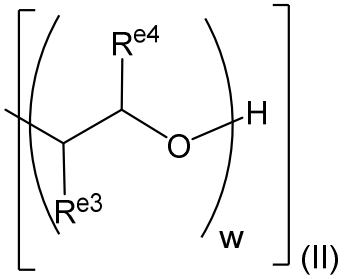
81. A (poly)ol block copolymer according to claim 80, wherein -A'- has the following structure:



(I)

wherein the ratio of p:q is at least 7:3;

and block B has the following structure:



(II)

and R^{e1}, R^{e2}, R^{e3} and R^{e4} depend on the nature of the epoxide used to prepare blocks A and B.

82. A (poly)ol block copolymer according to claim 81, wherein each R^{e1}, R^{e2}, R^{e3}, or R^{e4} is independently selected from H, halogen, hydroxyl, or optionally substituted alkyl (such as methyl, ethyl, propyl, butyl, $-CH_2Cl$, $-CH_2-OR_{20}$, $-CH_2-OC(O)R_{12}$, or $-CH_2-OC(O)OR_{18}$), alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl, preferably selected from H or optionally substituted alkyl.

83. A (poly)ol block copolymer according to any of claims 81-82, wherein R^{e1} and R^{e2} or R^{e3} and R^{e4} together form a saturated, partially unsaturated or unsaturated ring containing carbon and hydrogen atoms, and optionally one or more heteroatoms.

84. A (poly)ol block copolymer according to any of claims 78-83, wherein the starter residue depends on the nature of the starter compound, and wherein the starter compound has the formula (III):

$$Z\text{-}(R^Z)_a \qquad \text{(III)}$$

wherein Z can be any group which can have 1 or more, typically, 2 or more $–R^Z$ groups attached to it and may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, hererocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or Z may be a combination of any of these groups, for example Z may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group;

a is an integer which is at least 1, typically, at least 2, optionally a is in the range of between 1 or 2 and 8, optionally a is in the range of between 2 and 6;

wherein each R^Z may be –OH, -NHR', –SH, -C(O)OH, -P(O)(OR')(OH), $–PR'(O)(OH)_2$ or –PR'(O)OH, optionally R^Z is selected from –OH, -NHR' or -C(O)OH, optionally each R^z is –OH, -C(O)OH or a combination thereof (e.g. each R^z is –OH);

wherein R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, optionally R' is H or optionally substituted alkyl; and

wherein Z' corresponds to R^z, except that a bond replaces the labile hydrogen atom..

85. A (poly)ol block copolymer according to claim 84, wherein the starter compound is selected from monofunctional starter substances such as alcohols, phenols, amines, thiols and carboxylic acid, for example, alcohols such as methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, linear or branched C_3-C_{20}-monoalcohol such as tert-butanol, 3-buten-1-ol, 3-butyn-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, propargyl alcohol, 2-methyl-2-propanol, 1-tert-butoxy-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, 1-heptanol, 2-heptanol, 3-heptanol, 1-octanol, 2-octanol, 3-octanol, 4-octanol, 1-decanol, 1-dodecanol, phenol, 2-hydroxybiphenyl, 3-hydroxybiphenyl, 4-hydroxybiphenyl, 2-hydroxypyridine, 3-hydroxypyridine, and 4-hydroxypyridine, mono-ethers or esters of ethylene, propylene, polyethylene, polypropylene glycols such as ethylene glycol mono-methyl ether and propylene glycol mono-methyl ether, phenols such as linear or branched C_3-C_{20} alkyl substituted phenols, for example nonyl-phenols or octyl phenols, monofunctional carboxylic acids such as formic acid, acetic acid, propionic acid and butyric acid, fatty acids, such as stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, benzoic acid and acrylic acid, and monofunctional thiols such as ethanethiol, propane-1-thiol, propane-2-thiol, butane-1-thiol, 3-methylbutane-1-thiol, 2-butene-1-thiol, and thiophenol, or amines such as butylamine, tert-butylamine, pentylamine, hexylamine, aniline, aziridine, pyrrolidine, piperidine, and morpholines; and/or selected from diols such as 1,2-ethanediol (ethylene glycol), 1-3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexenediol, 1,4-cyclohexanedimethanol, dipropylene glycol, diethylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, polypropylene glycols (PPGs) or polyethylene glycols (PEGs) having an Mn of up to about 1500g/mol, such as PPG 425, PPG 725, PPG 1000 and the like, triols such as glycerol, benzenetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, trimethylol propane, polyethylene oxide triols, polypropylene oxide triols and polyester triols, tetraols such as calix[4]arene, 2,2-bis(methylalcohol)-1,3-propanediol, erythritol, pentaerythritol or polyalkylene glycols (PEGs or PPGs) having 4–OH groups, polyols, such as sorbitol or polyalkylene glycols (PEGs or PPGs) having 5 or more –OH groups, or compounds having mixed functional groups including ethanolamine, diethanolamine, methyldiethanolamine, and phenyldiethanolamine.

86. A (poly)ol block copolymer according to any of claims 57-85, wherein the (poly)ol molecular weight (Mn) is in the range 300-20,000 Da and the molecular weight (Mn) of block A is in the range 200-4000 Da, and wherein the molecular weight (Mn) of block B is in the range 100-20,000 Da, more typically, the molecular weight (Mn) of block A is 200-2000 Da , more typically 200-1000 Da, most typically 400-800 Da and/or the molecular weight (Mn)of block B is typically 200-10,000 Da, more typically 200-5000 Da.

87. A (poly)ol block copolymer according to claim 86, wherein the molecular weight (Mn) is measured by Gel Permeation Chromatography (GPC).

88. A (poly)ol block copolymer according to any of claims 57-87, wherein block A is a generally alternating polycarbonate (poly)ol residue.

89. A composition comprising the (poly)ol block copolymer of any of claims 57-88 and one or more additives selected from catalysts, blowing agents, stabilizers, plasticisers, fillers, flame retardants, and antioxidants.

90. A composition according to claim 89 further comprising a (poly)isocyanate.

91. A polyurethane produced from the reaction of a polyol block copolymer according to any of claims 57 to 88 or a composition according to claim 89 or 90 and a (poly)isocyanate.

92. A polyurethane comprising a block copolymer residue according to any of claims 57-87.

93. An isocyanate terminated polyurethane prepolymer comprising the reaction product of a block copolymer according to any of claims 57 to 88 or a composition according to claim 89 with an excess of (poly)isocyanate.

94. An isocyanate terminated polyurethane prepolymer comprising a block copolymer residue according to any of claims 57-88.

95. A composition according to claim 89 or 90, wherein the catalysts for the (poly)isocyanate and the polyol block copolymer reaction include suitable urethane catalysts such as tertiary amine compounds and/or organometallic compounds.

96. A composition according to claim 89 or 90, wherein a trimerisation catalyst is present.

97. A composition according to claim 89, wherein an excess of (poly)isocyanate, more typically, an excess of polymeric isocyanate relative to polyol is present so that polyisocyanurate ring formation in the presence of the trimerisation catalyst is possible.

98. A lubricant composition comprising a (poly)ol block copolymer of any of claims 57-88.

99. A surfactant composition comprising a (poly)ol block copolymer of any of claims 57-88.